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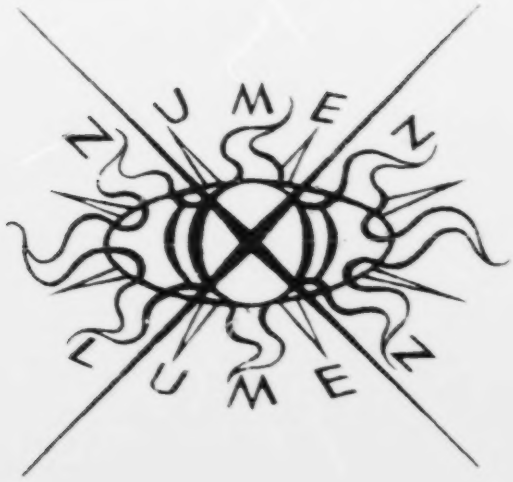

ALGICIDES

by
George P. Fitzgerald
UW Water Resources Center

Publication supported
by
Federal Water Quality Administration
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Soap and Detergent Association
U.S. Department of Agriculture
The University of Wisconsin

February 1971

The University of Wisconsin
Water Resources Center

Eutrophication Information Program

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Water Resources Center
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ABOUT THE AUTHOR --

For the past twenty years Dr. George P. Fitzgerald has conducted algal research at the University of Wisconsin with particular emphasis on algal nutrition and the chemical control of algae. He is presently a Research Associate with the Water Resources Center and previously held similar positions with the Engineering Experiment Station and the Botany Department.

Dr. Fitzgerald received a Bachelor of Science degree in chemistry from the University of Wisconsin in 1948, a Master of Science degree in botany from Wisconsin in 1949, and a Doctor of Philosophy degree in botany and biochemistry from Wisconsin in 1950.

From 1948-56, Dr. Fitzgerald studied the isolation, culture, nutrition and chemical control of problem-causing algae. This work was followed by several years of research to investigate the biological removal of algal nutrients from waste-water stabilization ponds. The effect of algae on BOD measurements was also studied extensively. More recent studies include the investigation of nutrient sources for algae and the compatibility of chemicals used to control algae in swimming pools. He has authored more than fifty scientific papers regarding the culture of algae, bioassays for available nutrients, in situ bioassays for the nutritional status of algae and aquatic vegetation, bioassays for toxic chemicals and factors which influence their effectiveness, and the compatibility of chemicals used for algal and bacterial control in swimming pools.

ALGICIDES

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ALGICIDES

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INTRODUCTION

Those concerned with lake management generally agree that the most acceptable long-term method of controlling undesirable growths of algae and rooted aquatic plants is to restrict the flux of plant nutrients to natural waters by controlling or eliminating the nutrient sources. However, many lakes have deteriorated to the point that preventive measures alone are insufficient, and direct action is required to gain relief from excessive algal growths. One approach to this problem is the use of algicides to either kill the algae or prevent their growth.

In recent years much concern has been expressed regarding the indiscriminate use of toxic chemicals in the environment; the controversy over DDT is an outstanding example. It is not the intent of this review to discuss the many ramifications of whether or not algicides should be used, but rather, this review is concerned with algicides themselves--what chemicals are used, how they are tested, and how effective they are when used in natural waters. Factors which influence their effectiveness and methods of application are also discussed.

Problems caused by algae can be related to either their presence alone or to the effects they may induce. Massive growths of planktonic algae can shorten filter runs in water treatment plants or cause beaches to become coated with repugnant green scums. Growths of filamentous algae, such as Cladophora or Pitnophora, can clog filter intake screens of water treatment plants, necessitate the closing of beaches because of extensive accumulations and subsequent decay, slow the flow of water in canals, and restrict boat travel on rivers when floating masses of algae accumulate. Filamentous algae in fish ponds can result in an imbalance between predator and prey species because the forage species hide in the algae and successfully evade the larger fish. The problem caused by algae

that probably affects the greatest number of people is the production of undesirable tastes and odors in potable water supplies, and this problem accounts for the greatest volume of algicide applications.

The primary objectives of algal control are to prevent the growth of obnoxious species or to cause a change in species composition to more desirable (or less obnoxious) species. It is generally easier to cause a change in algal species than it is to completely prevent the growth of all algae. An application of a selective algicide can virtually eliminate specific algae from a body of water and allow other forms to dominate. To prevent the growth of all algae a universally toxic chemical must be added at frequent intervals in order to maintain algistatic conditions. The key to practical algal control for a particular problem is to identify those species causing the problem and then determine the degree of control necessary to alleviate the condition.

Several general references give details of the modes of action or methods of application of some of the practical algicides in use (Hale, 1954; McCallan, 1956; Reddish, 1957; Owens, 1963; McKee and Wolf, 1963; Skidmore, 1964; Sladeckova and Sladeck, 1968; Mackenthun, 1969). Although many studies have been conducted to investigate the effectiveness and mode of action of various antibiotics on algae (Foter et al., 1953; Zehnder and Hughes, 1958; Hunter and McVeigh, 1961; Stepanek et al., 1962; Krauss, 1962; Perlman, 1964; Whitton, 1968), these studies will not be reviewed because large-scale applications have not yet become feasible.

EVALUATION OF ALGICIDES

Test Organisms

An obvious selection of test species for evaluating potential algicides is to use algae which are actually causing a problem. This is most readily done in the field. Fitzgerald et al. (1952) used tanks and lagoons and Stepanek et al. (1960)

used large plastic bags to contain lake waters and the algae to be studied. However, it is not always convenient or economical to work in the field. To study the effectiveness of many chemicals at various dosage rates, laboratory evaluations are a practical necessity. One approach is to transfer the indigenous organisms to the laboratory for testing, but this technique has the distinct disadvantage that these algae often die because they are not adapted to laboratory culture. The effect of algicides can then be measured only in terms of an increased death rate as compared to that which occurs in untreated control cultures. This complicates data analysis and limits the applicability of the test to those chemicals which kill algae very rapidly. For detailed, reproducible tests of toxic chemicals one is forced to make preliminary evaluations in the laboratory with species which are readily cultured.

Stock collections of algae are a convenient source of test organisms that are adapted to laboratory growth, but care still must be taken in selecting the particular species to be used in testing algicides for a specific problem. Considerable work has been reported in which algae which are taxonomically related to problem-causing algae were used but which, in actual fact, do not respond to certain chemicals in any manner related to that of the actual problem-causing organism. One such example would be the use of the readily cultured Coccochloris peniocystis and Nostoc muscorum to represent the bloom-forming blue-greens, Anacystis (Microcystis aeruginosa) and Anabaena circinalis; the two former species are relatively resistant to dichlone (2,3-dichloronaphthoquinone), but this chemical has been shown to be very effective in killing the latter problem-causing species (Fitzgerald et al., 1952; Fitzgerald and Skoog, 1954).

However, it has been established that certain groups of problem-causing algae do respond to particular chemicals in a similar manner. This is illustrated by the sensitivity of certain bloom-forming blue-green algae to copper: concentrations of 0.05 to 0.1 mg $CuSO_4.5\ H_2O$/liter will kill Microcystis aeruginosa, Anabaena circinalis, and Gloeothrichia echinulata, whereas more than 3 mg/liter are necessary to prevent the growth of the green alga, Chlorella pyrenoidosa, (Fitzgerald and Faust, 1963a, 1963b). It is obvious in this case that, if the problem-causing algae are the planktonic blue-greens, the

results of tests with Chlorella will grossly overestimate the required concentration of copper for treatment. Just because the planktonic blue-greens are particularly susceptible to copper and dichlone (Lange, 1944; Fitzgerald et al., 1952; Fitzgerald and Faust, 1963a) does not mean that they will be relatively more susceptible to other chemicals. A surfactant, alkylbenzene sulfonate (ABS), will prevent the growth of bloom-forming Aphanizomenon and Anabaena at a concentration of 5 mg/liter or less, but a concentration of 60 mg/liter of ABS only causes about 75% inhibition of the growth of either Microcystis aeruginosa or Chlorella (Fitzgerald, 1964b). Therefore, it is scientifically unsound to test only a single species of algae, and then predict that similar results will be obtained if the same concentration of a chemical is used on similar types of problem-causing algae. This practice is also cautioned against in the study of disinfectants (Ostrander and Griffith, 1964).

Culture and Test Media

After the appropriate test organisms have been selected, it is necessary to culture the algae so they are readily available. The principal objective of toxicity tests is to describe the reproducible toxicity of a chemical for a particular group of algae. The variability of results from test to test must be kept minimal. Factors, such as the physiological status of the algae and the amount of algae used, should be controlled so that, if they are important to a particular problem, they can be studied as separate entities. A simple approach is to grow the algae in the selected medium and add different concentrations of the chemicals to be tested when the algae have reached a reproducible stage of growth (Fitzgerald et al., 1952). If the test organism can be cultured reproducibly, a satisfactory technique is to use algae from rapidly growing stock cultures and inoculate the same known amounts into media containing various concentrations of the toxic chemical (Fitzgerald, 1960).

The amount of algae used in toxicity tests must be consistent from test to test because in some instances it has been shown that the amount of chemical required to inhibit the growth of algae is dependent on the amount of algae present (Fitzgerald, 1964b, 1967). This was illustrated by adding different initial concentrations of the green alga, Chlorella pyrenoidosa (Wis.

2005), to Allen's medium (Allen, 1952) and determining the concentrations of an industrial organic mercurial algicide required to prevent growth (Table I). When the initial concentration of

Table I. Concentrations of commercial organic mercurial algicide required to prevent the growth of different initial concentrations of Chlorella pyrenoidosa (Wis. 2005) in Allen's medium (Fitzgerald, 1964b).

Chlorella concentration (cells/ml)	Concentrations of Algimycin-MT4 to prevent growth (mg/liter)
150,000	½
300,000	1
600,000	2
900,000	3

Chlorella was increased from 150,000 to 900,000 cells/ml, the concentration of the algicide required for inhibition of the growth of Chlorella increased from 0.5 to 3 mg/liter. A fixed amount of toxicant per cell was required; the concentration was of secondary importance. This relationship has also been shown for bacteria (Fitzgerald and DerVartanian, 1967, 1969) and fungi (Richardson and Munnecke, 1964). Also, if the same quantity of Chlorella (7,500,000 cells) is suspended in different volumes of culture medium ranging from 25 to 250 ml, the amount of a stock solution (12.5 mg/liter) of a commercial quaternary ammonium algicide required to prevent the growth of the added Chlorella only increased from 1 ml for a 25 ml final volume of culture to 1.5 ml for a 250 ml final volume (Table II) (Fitzgerald, 1964b). Here again, the amount of toxicant per cell appeared to be of primary importance. The correlation between the amount of toxic chemical required to prevent growth and the amount of algae present, but lack of correlation between

the amount of toxic chemical required and the volume in which a given amount of algae are suspended, has been shown for products containing copper, organic mercury, and quaternary ammonium compounds.

Table II. Amount of commercial quaternary ammonium algicide required to prevent the growth of 7,500,000 Chlorella pyrenoidosa (Wis. 2005) cells in different volumes of Allen's medium (Fitzgerald, 1964b).

Culture volume (ml)	Volume of 12.5 mg/L stock solution of Algimaster-1963 to prevent growth (ml)
25	1
50	1
100	1
250	1.5

On the contrary, tests with two of the surfactants used in detergents, ABS and linear alkylate sulfonate (LAS), showed that there was a relationship between the amount of toxic chemical (ABS or LAS) required and the volume in which the algae were suspended: tests in 25, 50, 100 and 250 ml of media containing 7,500,000 Chlorella cells indicated that 0.5, 1.0, 1.5, and 3 mg, respectively, of LAS were required to prevent growth. Therefore, the type of chemical to be tested may influence the importance of some of the factors in designing toxicity tests. In all cases, some measure of the amount should be used consistently when comparisons are made of different chemicals or of the same chemicals at different times.

The nature of the algae used in toxicity tests will usually determine how much algae must be added to culture media to ensure consistent growth in test flasks. In evaluations of chemicals for the control of planktonic bloom-forming blue-green algae, initial cell densities equivalent to 1.5 million cells/ml

have been found to be satisfactory, whereas concentrations equivalent to 300,000 cells/ml were sufficient for algae representing the problem-causing species in swimming pools. It must be emphasized, however, that if a group of algae are to be compared as to their susceptibility to a toxic chemical, the same level of inoculation must be used for all species. Not all algae are easily counted with the use of a haemocytometer slide under a microscope, so absorbance measurements at 750 mμ have been used to measure cell concentrations. Relationships between cell counts and absorbance are established by diluting stock cultures of known cell concentrations. Cultures of filamentous algae can be measured readily by this method after they have been blended in mechanical mixers (with no measurable loss in viability). It is important to use an inoculum level which consistently gives good growth in the test cultures and to have a measure of this level so it can be reproduced.

The species of algae selected as the test organism will determine to some extent the culture media in which the tests are conducted. The planktonic blue-green algae seem to require relatively dilute alkaline media; a more concentrated neutral media can be used with algae found typically in swimming pools and water cooling towers. The chemistry of the medium used will affect the sensitivity of algae to toxic chemicals. For example, Phormidium inundatum, a blue-green alga causing problems in swimming pools, showed an increased resistance to copper sulfate when tests were run in Gorham's alkaline medium (Hughes et al., 1958) as compared to tests run in the neutral medium of Allen (1952) (Fitzgerald and Faust, 1964). Changes in pH also affect test results. Increased lytic activity of ammonium sulfate with increased pH values was noted in tests of Prymnesium parvum, the phytoflagellate causing mass mortalities of fish in ponds in Israel (Shilo and Shilo, 1953). Thus, care must be exercised in comparing results of tests in media of different compositions or pH values.

Since various media contain chelating agents to maintain the solubility of some of the components (a requirement based mainly on pleasing the esthetics of the worker rather than the alga involved (Goldberg, 1952; Fitzgerald, 1970)), the effect these agents have on the toxicity of the chemicals tested should be investigated. As early as 1905, Ellms (1905) reported that a mixture of leaf infusion and copper sulfate prevented a good

proportion of the copper from precipitating. Copper solutions prepared in the form of Fehling's solution in the glycerine-potassium hydroxide silk reagent, as well as aliphatic hydroxy acid solutions, were studied by Gelfand (1946). McIntyre (1949) suggested a mixture of copper sulfate and ammonium hydroxide for the control of algae in swimming pools. Both Eidsness (1953) and Swartz (1953) reported that copper sulfate is less effective than either copper citrate or copper acetate as an algicide in hard waters.

Citric acid is one of the chelating chemicals used in culture media (Gerloff et al., 1950), and its effect on the relative toxicity of copper to algae and fish is very informative. Citric acid is added to culture media to maintain the iron in solution, and has also been suggested for keeping copper from precipitating in natural waters (Gelfand, 1946). It has been shown that citric acid will prevent the precipitation of copper in algal culture media (Fitzgerald, 1960; Fitzgerald and Faust, 1963a) without affecting its toxic properties; a concentration of 1 mg/liter of $CuSO_4 \cdot 5\ H_2O$ was found to prevent the growth of Chlorococcum sp., a green alga which causes problems in swimming pools, whether the copper was 78% soluble (in the presence of citric acid) or only 8% soluble. In addition, 1/2 mg/liter was found to be ineffective in both situations (Fitzgerald and Faust, 1963a). In contrast, studies of the effect of citric acid on the toxicity of copper to the bluntnose minnow (Hyborhynchus notatus) and several sunfishes have shown that a concentration of 0.5 mg/liter of $CuSO_4 \cdot 5\ H_2O$ would kill about 50% of the fish tested within 24 hours, whereas solutions containing 500 mg/liter of $CuSO_4 \cdot 5\ H_2O$ and 1,000 mg/liter of citric acid at either pH 6 or 8.5 did not kill any fish within 24 hours (Fitzgerald, 1963). It is apparent, therefore, that citric acid can keep copper in solution in alkaline waters without affecting the toxicity of the copper towards algae, but prevents the toxicity of copper to fish. These results suggested the possibility of using chelating agents to develop long-term algicides until further study indicated that bacterial degradation of citric acid and certain other chelating agents allowed the copper to precipitate after a few days (Fitzgerald and Faust, 1965).

Other chelators suggested for use in plant culture media have been polyamino-polycarboxylic acids, some of which are

ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA), N-(2-hydroxyethyl)iminodiacetic acid (HEIDA), and nitrilotriacetic acid (NTA). Since these products have also been suggested as possible replacements of the phosphorus compounds used in detergents, there is added interest in their possible effect on the toxicity of copper in water which may become contaminated with future detergents. A summary of tests to determine the effects of these chelators when present in algal culture media at a concentration of 1 mg/liter is presented in Table III as the concentrations of $CuSO_4.5\ H_2O$ required to prevent the growth of either Microcystis or Chlorella. These two algae were selected for testing because Microcystis represents the algae that are very susceptible to copper treatments and are killed by relatively low concentrations; Chlorella represents algae that are prevented from growing but are not killed by copper (Fitzgerald, 1964b; Fitzgerald and Faust, 1963b).

Table III. The effect of different polyaminopolycarboxylic acid chelators on the toxicity of copper to Microcystis aeruginosa (Wis. 1036) and Chlorella pyrenoidosa (Wis. 2005).

Chelate added (1 mg/L)	Concentration of $CuSO_4.5\ H_2O$ required to be algistatic (mg/liter)	
	Microcystis	Chlorella
None	0.05	1
EDTA	0.8	2
HEDTA	$>^a$0.8	4
HEIDA	0.4	3
NTA	0.4	3

[a] $>$ means "more than."

In contrast to the results with citric acid, these data indicate that these chelators will reduce the toxicity of any copper used as an algicide if they are present in significant

amounts. The data also indicate that the use of EDTA in culture media used for toxicity tests could give erroneous results, at least as far as copper is concerned (Fitzgerald and Faust, 1963a).

Some culture media used for algae employ extracts of soil as sources of nutrients or chelators (Starr, 1964; Matulova, 1964; Gorham et al., 1964). Such natural chelators (Schatz et al., 1964) have also been shown to reduce the toxicity of copper. When the bloom-forming blue-green alga, Anabaena circinalis, was tested in Gorham's medium (minus the EDTA) (Hughes et al., 1958), it was found that 0.05 mg/liter of $CuSO_4.5\ H_2O$ would prevent growth, but in the presence of soil extracts, concentrations of at least 0.2 mg/liter of $CuSO_4.5\ H_2O$ were required. It is apparent, therefore, that considerable care must be taken in selecting media or additives when evaluations of algicides are to be made.

Excessive uptake of toxicants also complicates the testing of algicides. Just about any toxic material added to a culture will be removed from solution because in the process of affecting algal growth it has to be incorporated into some vital function with which it will interfere. However, algae can take up toxicants in amounts far in excess of those necessary to inhibit growth. This was illustrated in the case of the toxicity of silver to Chlorella (Table IV). When three sources

Table IV. The detoxification of silver by Chlorella pyrenoidosa (Wis. 2005) in Allen's medium.

Silver source	Concentrations (mg/liter) required to prevent growth	
	After first inoculation[a]	After second inoculation[a]
Algaedyn[b]	10.0	[c] >160
1% $AgNO_3$	7.5	>160
1% Ag_2SO_4	7.5	>160

[a] 300,000 Chlorella cells/ml of final volume

[b] 0.8% colloidal silver

[c] > means "more than."

of silver (a commercial algicide and 1% solutions of silver sulfate or silver nitrate) were tested, it was found that 7.5 to 10 mg/liter of the algicides would prevent the growth of Chlorella. However, if the same amount of Chlorella was re-added to the cultures 2 to 11 days after the first inoculation, the growth of the second inoculum was not inhibited even in cultures originally containing 160 mg/liter of any of the sources of silver (Fitzgerald, 1967). Therefore, if for some reason (i.e. poor mixing) a portion of the cells is not exposed to the toxicant within a relatively short time, other cells can take up excess amounts, and those unexposed will grow as if the toxicant had never been present. This phenomenon may be of considerable importance in field applications and probably accounts for some research results which indicate that certain algicides inhibited growth for one week but showed no inhibition after three weeks.

Algistatic versus Algicidal Activity

Of more significance than the length of incubation of treated algal cultures before deciding final results have been achieved, is the question of whether the algae are dead (algicidal effect) or merely prevented from further growth (algistatic effect). Many earlier articles did not make any such distinction (Fitzgerald et al., 1952; Fitzgerald, 1957, 1959, 1960, 1962; Palmer and Maloney, 1955) and labeled chemicals algicidal at certain concentrations which, in fact, were only tested by algistatic procedures. The importance of distinguishing between chemicals that kill algae and those that merely prevent their growth at a specific concentration is demonstrated by the factors involved in the chemical control of algae in swimming pools (Fitzgerald and Faust, 1963b, 1964).

In swimming pools which have filtration apparatus, any chemical added that is insoluble, breaks down to insoluble products, or is adsorbed to the filter medium, will be removed from the water at rates dependent on the effectiveness of the filter and the number of times the water is filtered each day. It has been pointed out (APHA, 1957) that 95% of the suspended matter in a swimming pool will have been removed at the end of three turnovers. Therefore, it is important to determine: (1) if a chemical inhibitory to the growth of algae is removed

by the action of a pool filter, (2) how long a contact time between the chemical and algae is necessary for the chemical to affect the growth of the algae, and (3) whether the effect of the chemical on the algae continues after the chemical has been removed from the environment (algicidal effect) or if the algae can revive and grow once the critical concentration of the chemical has been lost from solution (algistatic effect).

The determination of the concentration of a chemical required for the prevention of the growth of a particular group of problem-causing algae is relatively simple, because increasing concentrations can be added to cultures and, after incubation, the cultures that didn't visibly grow had algistatic concentrations of the chemical present. The ease of this method has enabled various workers to test great numbers of potential algistats (Fitzgerald et al., 1952; Jansen et al., 1958; Perlman, 1964; Marvin and Proctor, 1964).

To test the algicidal properties of a chemical, one must decide whether to vary the concentration of the chemical or to vary the contact time. Figure 1 is a sketch which illustrates the combinations of exposure time and toxicant concentrations necessary to produce lethal results. In general, there is some minimum exposure time necessary for organisms to take up a lethal dose of the toxicant, and also, there is some minimum concentration that can be tolerated indefinitely. Within limits, then, it is possible to adjust the toxicant concentration or the contact time to yield the most economical application.

In swimming pools, chemicals may only be present for a limited time due to losses by adsorption on swimming pool filters, and this limits the contact time that would be practical (Bussy, 1949; Jung, 1954; Fitzgerald, 1960, 1962, 1963). For this reason a four-hour contact time has been used for tests of swimming pool algicides (Fitzgerald and Faust, 1964). For the control of algae in canals and irrigation systems a one-hour contact time has been used (Otto and Bartley, 1966). The exposure time that can be maintained in practice may be as important in economic decisions as the concentration of chemical that is required.

To determine if a concentration of chemical is algistatic or algicidal, samples of algae with various periods of exposure

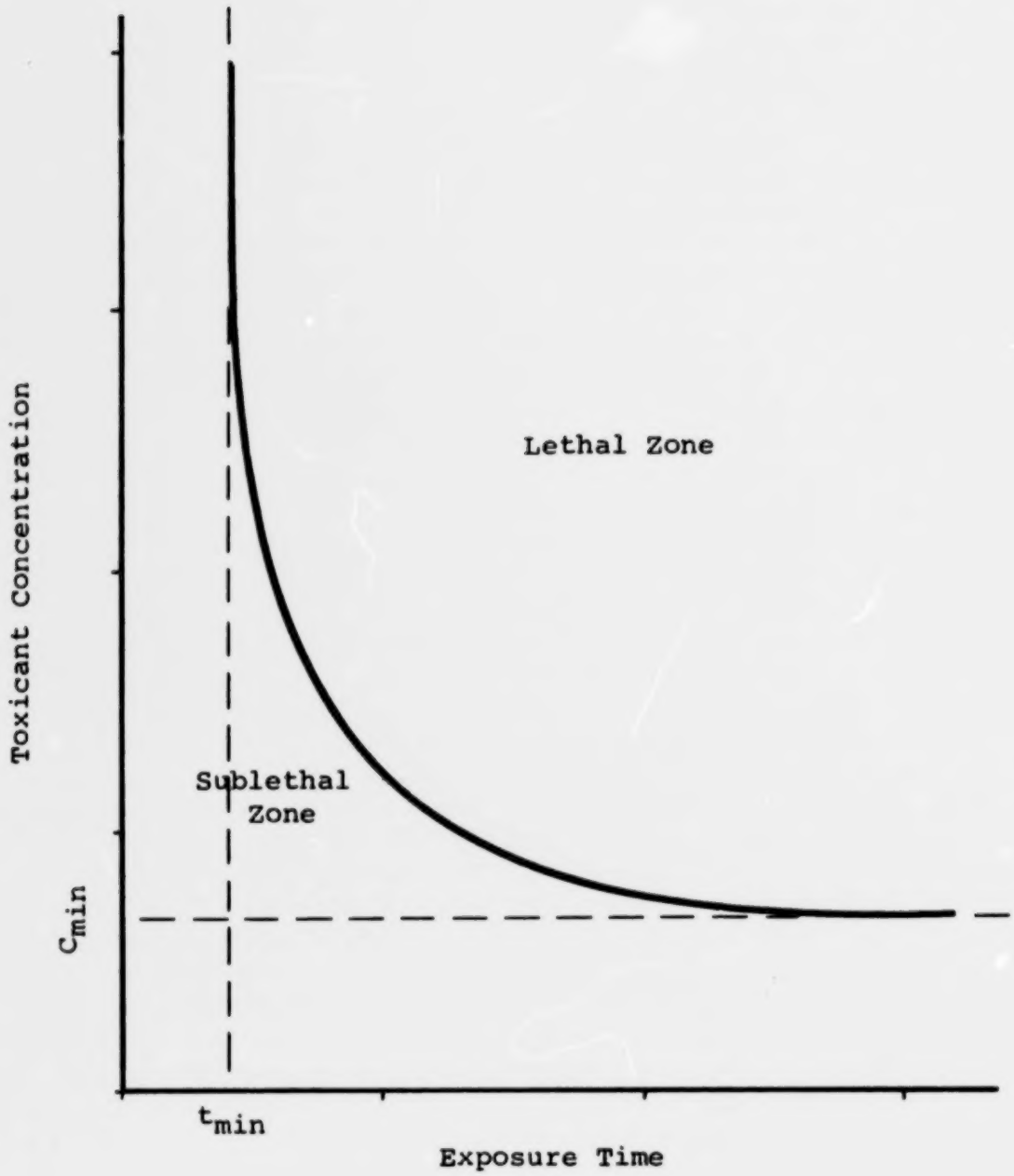

Figure 1. Combinations of exposure time and toxicant concentration necessary to produce lethal results.

should be transferred to sterile medium and then allowed to grow. If no growth occurs in a reasonable time, the dose would be considered algicidal. The size of sample to be subcultured may vary from the total sample (Otto and Bartley, 1966) to 1 ml of 25 ml or more (Fitzgerald and Faust, 1963b, 1964; Ukeles, 1962). Phillips and Warshowsky (1958) and Otto et al. (1960) have discussed the "criteria of death" from the point of view of how many cells should be tested before deciding some chemical concentration was "cidal." They also discuss whether some kind of detoxification agent should be present in the subculture medium as is commonly done in tests for bacteria in the presence of chlorine. For some chemicals, tests have indicated that detoxifying chemicals in subculture media are not necessary; subcultures grew when contact times were less than 4 to 12 hours with certain quaternary ammonium products or in less than 10 minutes with dichlone or the organic mercury products (Fitzgerald et al., 1952; Fitzgerald and Faust, 1963b). However, in some instances, the copper or silver carried over in subcultures was found to be algistatic unless EDTA or thioglycollic acid was present in the subculture medium (Fitzgerald, 1967). Therefore, the simple subculture technique can be varied by using different times of contact, subculturing in detoxifying media, or washing of treated algae as done by Otto and Bartley (1966).

Other methods which have been used to evaluate algicides are based on measurements of respiration, photosynthesis, or the chlorophyll content of the algae. Methods testing diffusion of the toxic chemical and subsequent effects on algae have also been described. There are obvious advantages of methods such as these which give results in relatively short periods of time. These tests may be carried out in situ, and there is the practical advantage that the suitability of the chemical for the control of the problem algae is measured directly under the existing conditions (Cervenka et al., 1959; Stepanek and Cervenka, 1961). Even in the laboratory, methods which yield a rapid evaluation of the effect of added organic compounds (Geoghegan, 1957) or physical conditions (McBrien and Hassall, 1967) are of considerable value. These short-term methods are most suitable for certain chemicals which rapidly affect respiration or photosynthesis (Beddow et al., 1968; Phelps and Schlichting, 1968) or the chlorophyll content of algae (Price and Estrada, 1964; Zweig et al., 1968; Sikka and Pramer, 1968). It must be borne in mind, however, that the equipment for the above tests is highly specialized, and the results obtained are dependent on relatively high concentrations of algae reacting to the presence of chemicals only in the manner the technique measures.

Techniques which depend upon the diffusion of a toxic chemical can be applied to practical problems, such as the formulation of anti-fouling mixtures (Christie and Crisp, 1963), but great caution must be used with the general application of these techniques because they give positive results only for chemicals not affected by the conditions of the tests. In studies of antibiotics, Foter et al. (1953) and Shilo (1965) have described variations of the agar plate techniques which require the diffusion of the toxic chemical through solidified media. Foter et al. placed filter paper discs containing antibiotics on inoculated agar, and Shilo added test chemicals to penicillin cups embedded in agar which had been inoculated with algae. Results were reported in terms of the diameter of the inhibition zones around the sources of added chemicals. A series of tests related to the diffusion of toxic chemicals were carried out to investigate problems involving the precipitation of copper or sorption of quaternary ammonium compounds as well as the effect of agar on toxicity tests. The concentration of various chemicals required to prevent the growth of Chlorella was determined in 25 ml of Allen's medium (Allen, 1952), Allen's medium plus 1 gram of powdered cellulose (thin-layer chromatography grade) or 1 gram of diatomaceous filter medium, or Allen's medium solidified with 1.5% agar. In addition, determinations were made of the concentration of chemicals required to cause a 1/2 to 1 cm zone of inhibition of growth around 0.1 ml of chemical on a glass-fiber filter pad (2.1 cm) on inoculated agar. The chemicals tested were copper sulfate, silver nitrate, and a commercial algicide containing quaternary ammonium compounds. The results of the tests are summarized in Table V.

Copper, organic mercury and quaternary ammonium products were required at concentrations of 1 to 2 mg/liter and silver nitrate at a concentration of 0.1 to 0.15 mg/liter to prevent the growth of Chlorella in the normal algistatic tests in liquid cultures. When agar, cellulose, or diatomaceous filter medium was present, two to sixteen times more of the products were required to be effective as algistats. When 0.1 ml of different concentrations of the chemicals were placed on glass-fiber filter discs on an agar plate surface, it was found that apparently none of the silver left the disc when concentrations as high as 5000 mg/liter were tested, but this concentration for tests using copper and quaternary ammonium products was

Table V. Effect of different methods of testing on the algistatic properties of chemicals to Chlorella pyrenoidosa (Wis. 2005).

Chemicals tested	Range of concentrations required (mg/liter)				
	To prevent growth in[a]				To cause ½-1 cm inhibition zone around 0.1 ml on filter pad[b]
	Liquid	Liquid + 1 gram cellulose	Liquid + 1 gram diatomaceous filter medium	Solidified 1.5% agar	
Copper sulfate ($CuSO_4.5H_2O$)	1-2	8	4	32	5000
Silver nitrate ($AgNO_3$)	0.1-0.15	0.3	0.3	0.6-0.8	[c] > 5000
Organic mercury algicide (Algimycin-200)	1-2	4	4	4-8	250
Quaternary ammonium algicide (Exalgae L.C.)	2	8	4	6-12	1000-5000

[a] 25 ml Allen's medium/50 ml Erlenmeyer flask; 300,000 Chlorella cells/ml.

[b] 10 ml Allen's medium plus 1.5% agar/Petri plate; 300,000 Chlorella cells/ml.

[c] > means "more than"; signifies highest concentration tested was not algistatic.

high enough to cause distinct zones of inhibition, and 1/20 of this concentration was sufficient in the case of the organic mercury product. The effect of the presence of powdered cellulose and diatomaceous filter medium demonstrates how sorption processes could affect the effectiveness of algicidal chemicals without actually removing them from the algal environment. The loss in toxicity when the algae and chemicals were dispersed in agar does not differentiate between effects of unwashed agar on toxicity tests (Hanus et al., 1967) or sorption and lack of diffusion of the chemicals to the algae. However, these effects demonstrate how tests involving such factors could discriminate against certain chemicals known to be either effective algicidal or algistatic products.

The use of mixtures of chemicals or sequences of chemical treatments for algae control is of special interest when dealing with chemicals that are especially effective as algistats. The substituted phenylureas (monuron and diuron) and triazine derivatives (atrazine and simazine) have been shown to be very effective for long-term control of problem-causing algae (Fitzgerald, 1957; Walker, 1965; Frank, 1966; Lawrence, 1968; Snow, 1963; Bussy, 1969), but are most effective when applied before the problems occur. Therefore, the preliminary use of algicidal chemicals and subsequent use of long-lasting algistats appear to be possible approaches in the future.

FACTORS IN ALGICIDE APPLICATIONS

Physical Losses

Characteristics of a particular algal problem influence not only selection of the methods for evaluating potential toxicants but also, place restrictions upon methods of application. Many chemicals can be dissolved or dispersed in a body of water which has an algal problem, but account must be made of the reaction of the environment on the toxic chemical because this determines how long an effective concentration can be maintained. The effect of alkalinity on the solubility of copper is an example. A number of studies have been made on the effect of water hardness or alkalinity upon the solubility of copper. Ellms (1905) was probably the first to show that

in hard water, copper was removed from solution as a colloid and later separated completely as a precipitate. He found that 40% to 50% of the copper added to hard water could be removed by filtration within 10 to 15 minutes; 75% to 95% could be removed after 3 hours elapsed. After 24 hours, no copper was detected in the filtrate. Monie (1944) developed a technique which related the alkalinity of the water to the amount of copper necessary for effective algicidal action. In midwestern states, where copper is used for the practical control of algae, dosage rates are adjusted routinely for alkalinity. Bartsch (1954) and Mackenthun (1969) suggested that the amount of copper sulfate used for algal control in lakes be changed from 0.9 pounds per acre-foot in waters with methyl orange alkalinites below 50 ppm to 5.4 pounds of copper sulfate per acre when dealing with waters of greater alkalinity.

Tests reported by Fitzgerald (1960) demonstrated how waters of different qualities will affect the solubility of inorganic copper (from copper sulfate). It was shown that if the pH of the water is low enough (pH 4), the alkalinity or hardness of the water had no effect on the solubility of the copper. However, at pH 7, the alkalinity or hardness exerts a considerable effect on copper solubility. Tests indicated that the commercial forms of chelated copper varied in their ability to maintain copper in solution, depending on the chemical characteristics of the water. In general, algae which require longer exposures to copper for effective inhibition can be controlled by the use of commercial mixtures that maintain the copper in a soluble, but effective, form as long as there is some biologically active chemical not removed by the algae.

Silver has also been shown to precipitate under the conditions to be expected in swimming pools and some natural waters. In the presence of 12 mg/liter chloride, the filtration apparatus in swimming pools may remove from 25% to more than 75% of the added silver in one recycling period (Fitzgerald, 1967). The concentrations of chloride in swimming pools varies considerably; average values range from 80 mg/liter for indoor pools with low loads to 250 mg/liter for outdoor pools with high loads (McLean et al., 1961, 1962).

In addition to losses by precipitation, chemicals applied as algicides have been observed to lose effectiveness by adsorption, vaporization, and chemical inactivation. The loss of quaternary ammonium compounds by adsorptive processes has been studied in the laboratory and the field. It was shown by Jung (1954) and Fitzgerald (1962, 1963) that these compounds were removed from swimming pool waters by adsorption on sand filters, whereas an organic mercury algicide was not. The effect of swimming pool filtration on quaternary ammonium algicides was also confirmed by Mickus and Hovden (1967).

Adsorption also influences the effectiveness of silver. Some studies on the use of silver as a bactericide have suggested that bactericidally significant quantities of silver were adsorbed onto glass, polyethylene, fused quartz, membrane filters, and other surfaces (Chambers and Proctor, 1959, 1960; Chambers et al., 1962). However, Wuhrmann and Zobrist (1960) considered pyrex glass to be incapable of adsorbing enough silver to be significant in bactericidal studies. When concentrations of different silver sources (as much as 12 times those required for algistatic activity) were tested in vessels of pyrex, polystyrene, or glass coated with swimming pool paint, no residual effects on algae were detected (Fitzgerald, 1967). Without question, adsorptive processes can influence the results of some tests and practical uses of algicides, but not enough is known about the factors involved.

When the loss of activity of a toxic chemical occurs, it is difficult to determine exactly what is causing such loss. Volatilization of toxic chemicals is not commonly thought to be a factor in the loss of biocidal activity, but Yamada et al. (1969) have suggested that volatilization may account for the loss of mercury compounds added to synthetic activated sludge in sewage plant studies. Also, Otto and Bartley (1966) have pointed out the loss of acrolein by volatilization in algicide applications. Losses due to chemical inactivation by reactions taking place in the environment of algae are much easier to document.

There is a considerable amount of literature regarding substances present in natural waters which inhibit the action of chemicals that are toxic to algae. The effect of hardness, especially calcium, in reducing the toxicity of some metal

cations to aquatic organisms has been known since the work of Ringer (1897). This phenomenon is known as antagonism. In certain cases this effect with calcium is thought to be due to a reduction in the permeability of cell membranes to toxic compounds (Skidmore, 1964). Despite a lack of complete understanding of the processes taking place, the effects of hardness on reducing the effectiveness of quaternary ammonium compounds as bactericides have been well documented (Ridenour and Arbruster, 1948). The effects of hardness on reducing the toxicity of zinc to fishes have been reported by Doudoroff and Katz (1953) and Mount (1966). Although zinc is known to affect the composition of algal communities (Williams and Mount, 1965), it is not known if the effect of hardness on its activity to algae is the same as for fishes. Hardness has also been shown to decrease the toxicity of silver to bacteria (Wuhrmann and Zobrist, 1960), but not the toxicity of ethyl mercury phosphate to trout (Amend et al., 1969).

Another group of inorganic constituents which reduce the toxicity of potential algicides are the halides. The effect of halides is a pertinent subject inasmuch as silver has been used in the analysis of chloride, and chlorides have reduced the solubility of silver in some toxicity tests. However, as was found to be the case with the green alga, Chlorella, (Fitzgerald, 1967), chloride has been shown not to interfere with the toxicity of silver to bacteria (Wuhrmann and Zobrist, 1960) or fungus spores (Miller and McCallan, 1957). Bromide has been shown to partially affect the toxicity of silver to algae and fungus spores, and iodide drastically reduces the toxicity of silver to algae and fungus spores. For bacteriological analyses of water samples from swimming pools treated with silver, Sawamura et al. (1965) have suggested the addition of sodium iodide to stop the effects of silver, much the same as thiosulfate is used to stop the action of chlorine. It would seem that algae, bacteria, and fungus spores can compete with chloride for silver ions, partially compete with bromide, but cannot compete with iodide. The use of silver as an algistat in swimming pools treated with bromine or iodine is, therefore, of doubtful value.

Detoxification

Besides the problems related to losses in effectiveness of algicides due to inorganic reactions, the effects of organic chemicals that might be present in algal environments must be taken into account. Fogg (1962) and Lefevre (1964) have reviewed the production of extracellular organic materials by algae and have described some of the effects of this production on the algal environment. Fogg pointed out that as much as 45% of the organic matter produced by algae may appear as extracellular products. These extracellular products can be in the form of many dissolved organic chemicals, depending upon the algal species and environment involved. The organic matter can also be in the form of a protective layer of mucilage. An example of an alga that can grow in a protective layer of mucilage or slime is the blue-green alga, Phormidium retzii, which is known to be very resistant to treatment in some situations (Fitzgerald, 1959). To illustrate the mucilage that encloses certain algae, a few filaments can be suspended in a thin suspension of black drawing ink. The ink particles accumulate on the mucilage and emphasize its presence. The mucilage which surrounds the filaments could protect them from the action of chemicals that are adsorbed or detoxified by the surrounding sheath material.

Even without the secretion of a mucilaginous sheath around its filaments, it is possible for an algal colony to be protected from the action of toxic chemicals by growing in dense mats. An example of this is the blue-green alga, Phormidium inundatum, called Black Algae in California where it may be found in swimming pools (Fitzgerald, 1959). The dense, tightly packed filaments of this alga on the outer surface of the colony can protect the cells in the center from the action of certain toxic chemicals by adsorptive processes or detoxifying reactions.

Considering the dense algal blooms which occur in some fertile lakes, it is apparent that many organic compounds which reduce the effectiveness of algicides could be present. Possible reactions have been presented in studies of antagonism or reversal of toxic chemicals. The heavy metals and quinones, in general, have been shown to be detoxified by reactions with glutathione, cysteine, and other sulfhydryl compounds (Fildes, 1940; Colwell and McCall, 1946; Yoder, 1951; Phillips and

Warshowsky, 1958; Boney et al., 1959; McNew, 1960; Owens and Blaak, 1960; Merrifield and Yang, 1965). These reactions could result in the formation of new, less toxic chemicals, as in the cases with quinone-type compounds, or could reduce toxicity by chelation. The latter process has been shown to account for the antagonisms of copper toxicity to plant disease organisms (McNew, 1960) and for the tolerance to copper by plants in copper swamps (Dykeman and DeSousa, 1966). Fogg and Westlake (1955) have shown that extracellular polypeptides excreted into the culture medium by the blue-green alga, Anabaena cylindrica, affected the toxicity of added copper. More than 16 mg of copper per liter were required for death in the presence of the polypeptide (7.9 mg N/liter), whereas in the absence of polypeptides, this alga was killed by approximately 3 mg copper per liter. It appears that in some instances, the lack of effectiveness of certain algicides has been attributed to the development of resistance, when in fact, the reduction in toxicity could have been caused by extracellular products.

Development of Resistance

With increased usage of a chemical for algal control, there is an increased chance that resistant strains of algae will develop. For example, strains of algae which have become resistant to the chemical, 3-(p-chlorophenyl)-1,1-dimethylurea (monuron), have been identified (Fitzgerald, 1964b). The amount of monuron required to prevent the growth of five species of algae was tested in routine toxicity tests in Allen's medium (Allen, 1952). The algae used as inocula (300,000 cells/ml in final volume) were three strains of Lyngbya versicolor (Wis. 1034, 1090, 1092) and two strains of Phormidium autumnale (Wis. 1054 and 1091). Strains 1034 and 1054 had been maintained in the Wisconsin algae collection for 3 to 5 years, whereas strains 1090, 1091 and 1092 were isolated a short time prior to the test from aquaria treated previously with monuron. After approximately two weeks of incubation the results were recorded and are summarized in Table VI. Normally, 1 to 4 mg/l of monuron is sufficient to kill algae (Fitzgerald, 1957; Maloney, 1958; Shilo, 1965; Bussy, 1969) and 1 mg/l prevented growth of strains 1034 and 1054. However, those strains which had been exposed to monuron previously, exhibited considerable resistance to the toxicant; concentrations in excess of 50 mg/l were required to prevent growth of strains 1091 and 1092. The exact cause of this resistance is

not known; it may have been caused by reactions taking place inside the algae, lack of permeability to the chemical, or to extracellular products which detoxified the chemical.

Table VI. Comparison of the resistance of some strains of blue-green algae to the toxicity of 3-(p-chlorophenyl)-1,1-dimethylurea (monuron).[a]

Algae tested	Concentration of monuron required to prevent growth (mg/liter)
Lyngbya versicolor (Wis. 1090)	[b]>24
" " (Wis. 1092)	>50
" " (Wis. 1034)	1
Phormidium autumnale (Wis. 1091)	>50
" " (Wis. 1054)	1

[a]Allen's medium (Allen, 1952); initial algal concentration approximately 300,000 cells/ml.

[b]> means "more than."

The toxicity of another compound, 3-amino-1,2,4-triazole, with similar algistatic activities has been shown to be reversed by the addition of purines (Wolf, 1962).

All in all, there have been few cases of unsuccessful algicide treatments reported as being due to developed resistance on the part of the problem algae (Moyle, 1949), but several cases have been reported where environmental factors were shown to be involved (Allen, 1966; Fitzgerald, 1962, 1963, 1964b, 1967).

Synergism

Not all chemical reactions with potential algicides reduce the toxicity of the product. There is always a search for chemicals which when added simultaneously will cause the resulting toxic effect to be greater than predicted (synergism). The

review by Skidmore (1964) points out that mixtures of copper and zinc are synergistically toxic to various species of fish. Since the toxicity of zinc and copper to fish may not be due to interference with the same vital function in algae, it is not necessarily true that they would be synergistic when tested as algicides. This was found to be the case when the algistatic properties of copper, in the presence or absence of added zinc, were tested on the bloom-producing blue-green alga, Microcystis aeruginosa (on which copper is a very effective algicide), and on the green alga, Chlorella pyrenoidosa (on which copper is merely algistatic). With Microcystis it was found that the same concentration of copper (0.05 to 0.075 mg $CuSO_4.5\ H_2O$/liter) was required to prevent the growth of 1,500,000 cells/ml regardless of the addition of zinc at Cu:Zn ratios of 1:1, 1:2, 1:4 and 1:6. Similarly, a concentration of copper of 1 mg $CuSO_4.5\ H_2O$/liter was sufficient to prevent the growth of 300,000 Chlorella cells/ml whether 0, 0.5, or 2 mg $ZnSO_4.7\ H_2O$/liter were present. Thus, no synergism between copper and zinc was detected. Since the effect of hardness on the toxicity of zinc and on the possible synergism of zinc with copper was not tested, it is possible that these two products may be synergistically toxic in certain soft-water situations.

It would appear likely that synergistic reactions would occur when treatments with silver and other heavy metals are combined, since silver is known to increase the uptake of mercury by fungus spores (Miller, 1956; Miller and McCallan, 1957) and to act synergistically with copper against Echinid larvae in sea water (Soyer, 1965). Thus, the suggestion by Cervenka et al. (1959) that a combination of copper and silver treatments be used (CA 350 denotes 300 µg Cu/liter and 50 µg Ag/liter) has been tested by a number of workers in Czechoslovakia (Stepanek et al., 1960; Kocurova, 1966; Moravcova, 1967). Moravcova conducted tests to determine the amounts of toxicants required to cause a 50% toxic effect on the filamentous green alga, Cladophora glomerata, and found that although 600 µg/l of copper and 200 µg/l of silver were required when used separately, CA 350 was sufficient when they were combined. When CA 350 was used in water reservoirs for the control of blue-green algal blooms it was found to be very effective; however, the regrowth of other algae was the same as when copper was used alone, and a later application of copper alone also appeared to be very effective (Kocurova, 1966).

Therefore, the addition of 50 µg/liter of silver to double the effectiveness of 300 µg/liter of copper is a questionable practice when the price of silver is more than 30-fold that of copper.

Since the toxicity of silver is similar to that of copper when tested with the bloom-forming blue-green alga, Microcystis aeruginosa, and silver is about 20 times more effective than copper for preventing the growth of the green alga, Chlorella pyrenoidosa, these algae provide an interesting pair for evaluating possible synergistic reactions. The concentrations of copper sulfate and silver nitrate required to prevent the growth of these algae were determined for each toxicant and for combinations of them. At least three tests were carried out with each alga, and a summary of the results is presented in Tables VII and VIII.

The same range of concentrations of copper sulfate and silver nitrate (0.025 to 0.075 mg/liter, depending on the test) was required to prevent the growth of Microcystis. As the concentration of silver nitrate was increased from 1/6 that of the copper sulfate to an equal amount, no increase in the toxicity of copper sulfate was found in any individual test. Therefore, there was no synergistic effect with silver nitrate on this bloom-forming blue-green alga which is readily killed by relatively low concentrations of copper sulfate (0.05 mg $CuSO_4.5\ H_2O$/liter, Fitzgerald and Faust, 1963a).

The concentrations of silver nitrate required to prevent the growth of Chlorella or Microcystis are remarkably similar (0.05-0.10 mg/liter). However, the amount of copper sulfate required for algistatic action on Chlorella is about 20-fold that of silver nitrate. As might be expected then, the addition of up to 6 times as much copper sulfate to silver nitrate solutions did not increase the algistatic properties of the silver.

From these results with an alga highly susceptible to both copper and silver and with an alga relatively susceptible only to silver, no synergistic action could be detected between copper and silver. Perhaps only under certain environmental conditions or with certain algal blooms would a synergistic effect take place. It is doubtful that the use of copper-

Table VII. Effect of silver on the algistatic properties of copper to the blue-green alga, Microcystis aeruginosa (Wis. 1036). (1,000,000 cells/ml Gorham's (-EDTA) medium)

Toxic chemical	Range of concentrations of copper sulfate required to prevent growth (mg/liter)
Copper sulfate ($CuSO_4.5\ H_2O$)	0.025-0.075
Silver nitrate	0.025-0.075[a]
Copper sulfate plus silver nitrate (6:1)	0.025-0.075
Copper sulfate plus silver nitrate (4:1)	0.025-0.075
Copper sulfate plus silver nitrate (1:1)	0.025-0.075

[a]Concentration of silver nitrate ($AgNO_3$)

Table VIII. Effect of copper on the algistatic properties of silver to the green alga, Chlorella pyrenoidosa (Wis. 2005). (300,000 cells/ml Allen's medium)

Toxic chemical	Range of concentrations of silver nitrate required to prevent growth (mg/liter)
Silver nitrate	0.05-0.10
Copper sulfate ($CuSO_4.5\ H_2O$)	1-2[a]
Silver nitrate plus copper sulfate (1:1)	0.075
Silver nitrate plus copper sulfate (1:4)	0.075
Silver nitrate plus copper sulfate (1:6)	0.05-0.075

[a]Concentration of copper sulfate

silver mixtures would be economically justified to control algae which are susceptible to copper alone, but it may be feasible to use the mixture on algae which are relatively more susceptible to silver.

The synergism between an organic mercury algicide and chlorine against bacteria has been established in both laboratory and field studies (Fitzgerald and DerVartanian, 1969; Black, 1968, unpublished data). It may be possible to apply similar combinations to algae. Also, the effectiveness of a commercial algicidal mixture containing copper has been shown to be due to a synergism between the active ingredients (Great Lakes Biochemical Co., 1969, unpublished). With further understanding of the factors required to bring about synergistic activity, it may be possible to prepare effective mixtures for particular algal problems and environmental conditions.

PRACTICAL USES OF ALGICIDES

To summarize the various chemical treatments used commonly to control algae, four types of problem areas will be discussed: water supply reservoirs and recreational lakes, fish ponds, swimming pools, and cooling towers. Although the same or similar algal species may cause problems in more than one of these categories, the different uses of the water dictate the required characteristics of algicides and methods of application that are appropriate.

Lakes and Water Supply Reservoirs

The greatest expenditure of funds for algal control has been made for treatment of water supply reservoirs and recreational lakes. Algal problems in water supplies affect all the users, and any restrictions on the volume of water available or changes in taste or odor cause immediate reactions from the public. The control of algal problems in water reservoirs is under the supervision of professional personnel who are keenly aware that their product will be evaluated in every household. Similarly, the control of obnoxious growths of algae in recreational waters is judged by the general public. Any massive growth of algae causes problems in either reservoirs or lakes.

The filamentous green algae, such as Cladophora, Pithophora, Spirogyra, or Hydrodictyon, have been known to restrict the flow of water into intake lines of water plants or even to impede navigation on rivers. The planktonic blue-green algae not only can grow profusely enough to give the water a definite green color but, because of their floating characteristics, can accumulate at the surface in thick repugnant green scums. Decomposition of this proteinaceous material can cause undesirable tastes and odors.

In addition to problems caused by massive growths, some algae cause problems at relatively low cell densities due to the special characteristics of the species. Algae that produce mucilaginous sheaths may cause filter clogging at lesser densities of growth than other algae because the mucilage provides greater bulk to the algal colony and is a material that is particularly "slimy." Although diatom shells (diatomaceous earth) are used in water filtration operations, growths of certain diatoms, such as some species of Fragilaria, can clog water plant filters because of their mucilaginous sheaths. There are also some algae that impart tastes or odors to waters even when their concentration in the water is relatively low (Rohlich and Sarles, 1949; Palmer, 1959).

The control of the floating blue-green algae, taste- and odor-producing algae, and some filter-clogging algae is usually accomplished by the application of copper sulfate. This chemical is highly specific for these kinds of algae and is very effective (Hale, 1925; Domogalla, 1926; Fitzgerald and Faust, 1963a; Fitzgerald, 1964a, 1964b, 1966; Mackenthun, 1969). The magnitude of copper sulfate treatments for the control of algae is illustrated by the fact that over 20,000,000 pounds of copper sulfate are used for this purpose per year (British Columbia Research Council, 1967; Phelps Dodge Refining Corp., personal communication, 1967). For instance, the City of Los Angeles alone has used approximately 2,000,000 pounds per year, and the City of New York approximately 1,200,000 pounds, while smaller cities use one to two carloads.

The concentration of copper sulfate used for algal control depends upon the particular problem. It can range from less than 0.5 mg/liter to more than 10 mg/liter (Domogalla, 1926; Mackenthun, 1969; Maletic, 1964; Fitzgerald, 1964a). It has

already been pointed out that the amount of algae, the presence of dissolved organic matter, and the alkalinity of the water will affect the concentration of copper required for effective control of algae.

The method of application depends on the size of the water body and the frequency of treatment. An investment of approximately $1,200 for a boat, motor, tank, and pump equipment is sufficient to spray about 230 pounds of copper sulfate per hour or to treat 40 acres per hour (Lueschow and Helm, 1967, personal communication). Where more complex systems are practical, a variety of systems may be used (Hale, 1925; Mackenthun, 1969; Anonymous, 1965). By adding a hopper with a worm drive, the dissolve-and-spray system can be modified to spray a slurry of algicide without waiting for the chemicals to dissolve. Blower systems can rapidly treat large surface areas with a light dosing of material. This system is used most efficiently when winds of 10-15 miles per hour aid in the distribution of the chemical. Approximately 10,000 pounds of copper sulfate can be applied in 4 or 5 hours on a day with favorable winds, but less than half this amount can be applied on a calm day.

Toxicants can also be distributed by adding chemicals to the propellor wash of outboard motors. Screened hoppers or belt conveyors are used to add the algicide. This method can be adapted to shallow, surface treatments by using finely ground copper sulfate or to deep-water treatments by using larger crystals which penetrate farther before dissolving. The use of air boats has been suggested for shallow areas where it is not desirable to stir up the bottom muds (Allen, 1966).

Helicopters or airplanes similar to those used for agricultural spraying have been used to apply copper sulfate at rates up to 2,500 pounds per hour (Anonymous, 1965; Decosta and Laverty, 1965). Regular applications from aircraft are especially advantageous for preventive treatments. However, Rosenberg (1964) has pointed out that the labor-saving prospects of aerial applications are not too important to water treatment facilities because algal control is just a part of the duties of the plant personnel.

The frequency of treatment of water reservoirs is sometimes based on observations of the algal populations, with the personnel in charge using past knowledge as to which algal species

are apt to cause trouble. Guseva (1941) in Russia used a system of laboratory cultures which would predict the growth of the algae likely to occur in a reservoir in the next five to seven days. Water works personnel could then either treat the reservoir for algal control or get prepared to combat the resulting taste and odor problems associated with the particular algal species. Some water utilities continuously treat the water entering the reservoir system and have found such treatments effective and economical (Anonymous, 1965; Hartman, 1961).

Most algal growths occur during the summer periods, but some algae which cause unpleasant tastes in the water are known to develop under the ice of water reservoirs (Anonymous, 1963). Resourceful personnel have developed methods of treating such problems by using bags of copper sulfate suspended through holes in the ice or by adding the chemical to inlets.

One of the problems with the use of copper sulfate is its specificity for only certain algae. It is quite successful in causing a change in the dominant species of algae in a body of water. If this is satisfactory, then copper sulfate can be used effectively. However, many times the algae replacing the original problem species cause problems of their own, and these latter algae are not controlled by usual treatments with copper sulfate (Fitzgerald and Faust, 1963a; Fitzgerald, 1965, 1966; Funk and Gaufin, 1965; Allen, 1966; Otto and Bartley, 1966). This problem of specificity is not limited to copper and also occurs with other algicides (Fitzgerald and Skoog, 1954). As a result, there have been several suggestions of chemicals that would be toxic to a larger variety of algae. Recent tests (Fitzgerald, 1964a, 1966) have shown that potassium permanganate is toxic to more algal species than is copper. The use of potassium permanganate will probably increase as the demand for general algicides becomes more important and as the price of copper increases.

The chemical control of algae in water reservoirs and recreational lakes has had a long history (Hassler, 1941; British Columbia Research Council, 1967), and many of the problems associated with the use of copper sulfate for this purpose have been pointed out. Some of these problems, such as precipitation and loss in activity by chelation with certain pollutants, could be overcome by the use of some organic mercury algicides which have been shown to be 100 times more effective than copper sulfate against Microcystis aeruginosa. How-

ever, because copper sulfate has been so successful in this field despite its many drawbacks, it will probably remain the main algicide of choice for this purpose for a considerable time.

Fish Ponds

Massive growths of filamentous green algae, such as Hydrodictyon, Pithophora, or Ulothrix, may cause problems in fish ponds because they interfere with the physical operations. Another problem is fish kills associated with blooms of blue-green or flagellate algae (Shilo and Shilo, 1953; Lawrence, 1954; Johnson, 1955; Snow, 1963; Shilo, 1965; Swingle, 1968). Since the growth of desirable algae in fish ponds is a necessity as a base for the food chain and to prevent the growth of undesirable weeds (Swingle et al., 1963), the chemical control of undesirable algae must bring about changes in the algal species rather than completely prevent the growth of all algae. Chemicals which have been shown to be effective for certain problems have been rosin amines, triazine derivatives (such as simazine), mercury compounds, and copper sulfate. Since the rosin amines and copper are both relatively toxic to fish and fish food organisms, they must be used with caution. Lawrence (1954) found that the most satisfactory and economical method of treating small ponds with the rosin amine, dehydroabietylamine acetate, was to treat the entire pond by placing the algicide on surface floats so that water currents would gradually disperse it. By using 3 to 4 pounds of a 70% paste of this product per surface acre on two floats for ponds of 2 to 3 acres, or a float for every 3 to 4 acres in larger ponds, the growth of undesirable Pithophora sp. was controlled without affecting the desirable phytoplankton. Snow (1963) controlled the growth of other undesirable filamentous algae, Hydrodictyon and Zygnema, by using simazine (2-chloro-4,6-bis(ethylamino)-s-triazine) at concentrations of 0.5 to 2 mg/liter. The growth of Chara sp. in rearing ponds for bass, sunfish, and channel catfish has also been successfully controlled by the use of simazine at 1 mg/liter (Whitley and Dillard, 1968). Attempts to control these types of filamentous algae by the use of copper sulfate have given unpredictable results, and in certain waters 1 mg/liter has been toxic to fish (Lawrence, 1968). It must be emphasized that in culture of fish, any chemical added to control problem algae or weeds should not harm the rate of

growth of the fish crop. Therefore, the use of fertilizers to stimulate the growth of desirable phytoplankton, which in turn will prevent the growth of undesirable filamentous algae or aquatic weeds, is a much preferred method of control (Swingle et al., 1963; Lawrence, 1968).

Although phytoplankton are generally preferable to rooted aquatic vegetation in fish ponds, there are occasions when chemical treatments are necessary to bring them under control. The problems phytoplankton cause may be due to algal toxins which kill the fish (Shilo, 1951) or to problem scums on surface waters. When algae concentrate at the surface of a pond, a combination of factors, including absorbed heat from sunlight, stratification of the pond water, and lack of photosynthetic oxygen production in deeper layers of the pond, contribute to the ultimate production of oxygen-deficient waters which can cause fish kills (Swingle, 1968). The blue-green alga, Microcystis, has been one of the common causes of this type of fish kill in both Israel and the United States. Partial eradication of this alga with copper sulfate allows deeper light penetration and distribution of oxygen to greater depths. Swingle (1968) and others have found that treatments with 0.75 pounds of copper sulfate per acre at one-week intervals are usually sufficient to control Microcystis. The use of ammonia and ammonium compounds to control a toxic flagellate, Prymnesium parvum, has been found to be effective during warmer months, but during the cooler part of the year mercuric products proved more effective (Sarig and Lahav, 1961). No matter what algicide is used, however, caution must be taken not to kill all of the algae at once because the resulting rapid decomposition of the algae could remove the dissolved oxygen from the pond and cause a total fish kill.

Swimming Pools

The control of the growth of algae in swimming pools is important from both esthetic and public health points of view. Repugnant green scums or slimy walls are certainly not conducive to enjoyable relaxation in a swimming pool. It is also reasonable to assume that if algae are in a pool, there probably is not a continuous, effective concentration of a bactericidal chemical present. When the bactericide, chlorine, is maintained at the recommended concentration of 0.5 mg/liter or more, there are usually no algal problems. The toxicity of chlorine and bromine to algae has been well established (Betzer and Kott,

1969), but some algal species isolated from swimming pools have been shown to be relatively resistant to the effects of chlorine (Beddow et al., 1968; Fitzgerald, 1968). Chlorine must be present at all times in order to prevent the development of algal colonies on the walls or apparatus in a swimming pool, because once massive layers of cells have developed the outer surfaces protect the inner layers from the oxidizing powers of the chlorine.

A major problem is the maintenance of effective concentrations of chlorine throughout the swimming pool. Pools are usually well designed for effective water circulation, chlorination, and filtration, but, if the proper operating procedures are not carried out, localized areas with little or no chlorine develop. Algae can then flourish in the bright light and relatively high nutrient waters of the pool. If chlorination is continuous but not uniformly distributed, colonies of filamentous blue-green algae, such as Phormidium inundatum, are selectively favored. This alga is called the "Black Algae" because of its characteristic growth as black spots on the walls of swimming pools. When chlorination is only intermittent any fast-growing alga could become dominant. Frequently the water is colored by growths of relatively resistant green algal species which are protected by mucilaginous coatings, such as Chlorococcum sp. (Wis. 1125). Therefore, unless the proper level of chlorine is maintained throughout a swimming pool, the use of algicidal chemicals will be necessary.

Iodine has been successfully used as a replacement for chlorine for the control of bacteria in swimming pools (Black et al., 1959; Marshall et al., 1963; Byrd et al., 1963), and Lackey et al. (1964) have indicated it to be effective also in preventing the growth of algae. However, Keirn and Putnam (1968) have indicated that the growth of algae in iodinated swimming pools is the largest drawback to its use, and have suggested that a program be carried out to evaluate algicidal compounds for use in conjunction with iodine.

Chemicals for use in swimming pools must be either effective algicides or long-lasting algistats. Because copper sulfate is only an effective algistat for the types of algae representing those causing problems in swimming pools, and as copper is readily lost from the water by precipitation, this chemical is not

effective in swimming pools (Bussy, 1949, 1952; Koch, 1954; Fitzgerald, 1964b; Fitzgerald and Faust, 1963a, 1963b, 1964). Silver products can also be lost from swimming pool waters by precipitation because of the chlorides normally found in swimming pools. In addition, if either bromides or iodides are present, the effectiveness of silver products as algistats is reduced or eliminated (Fitzgerald, 1967).

In contrast to the copper and silver products, quaternary ammonium and organic mercury products have been shown to be algicidal towards algae typically found in swimming pools. In order to be effective, though, these products must be present in algicidal concentrations for sufficient periods of time. Jung (1954) pointed out that the greater portion of quaternary ammonium compounds added to swimming pools was adsorbed on the filter sand, and this has been confirmed by Fitzgerald (1960, 1962, 1963) and Mickus and Hovden (1967). Quaternary ammonium products must, therefore, be added frequently enough to replace that portion which is lost to the swimming pool filter systems. Also, these products must be added in high enough concentrations to be algicidal because they will not last long enough to be effective algistats. The facts that the potential human pathogen, Pseudomonas aeruginosa, was found to increase in numbers in swimming pools treated with quaternary ammonium algicides (Keirn and Putnam, 1968), and that this organism is resistant to relatively high concentrations of quaternary ammonium compounds (Adair et al., 1969), leave some doubt as to the advisability of using such products in swimming pools even under conditions in which they could be effective algicides.

The organic mercury algicide used in swimming pools has been shown to be effective both as an algicide and as an algistat regardless of whether or not a filter is used (Fitzgerald, 1962; Fitzgerald and Faust, 1964). In addition, an organic mercury algicide has been shown in laboratory studies (Fitzgerald and DerVartanian, 1969) to be synergistic with chlorine against the bacteria, Pseudomonas aeruginosa, and against the total number of bacteria in actual swimming pool tests (Black, unpublished data, 1968). This type of product, however, is relatively easily detoxified by reactions with bacteria and algae and must be renewed to remain at effective concentrations in swimming pools.

A summary of the relative algistatic and algicidal properties of some of the products suggested for use as algicides in swimming pools is presented in Table IX. The recommended concentrations for initial treatment of swimming pools is compared to the concentration required to prevent the growth of the swimming pool blue-green alga, Phormidium inundatum (Wis. 1093) (300,000 cells/ml, Allen's medium). Also presented is the number of hours of treatment with the recommended concentrations of the products which were found to be required to kill the Phormidium.

These data indicate that all the products tested were effective algistats against this blue-green alga which causes problems in swimming pools. However, the copper and silver products are not algicidal even at relatively high concentrations and treatment times in excess of 24 hours (Fitzgerald, 1967, 1968; Fitzgerald and Faust, 1963b, 1964). The organic mercury and quaternary ammonium compounds killed the Phormidium, but excessively long contact times or higher concentrations would be required when quaternary ammonium products are used.

For the selection of a product for use in the control of the growth of algae in swimming pools without a filter system, chemicals can be compared for their relative effectiveness in preventing the growth of algae. If the swimming pool has a filter system, products can be selected on the basis of the amount of chemical required to kill algae within the length of time the product could be expected to be present at the minimum concentration for algicidal activity. Alternatives to the latter selection would be to: (1) select a chemical on the basis of its relative ability to prevent the growth of algae, and then turn off the filter system for 12 to 24 hours after each addition to give it sufficient time to be effective, or (2) select a chemical that is not affected by the action of the filter system. In any case, the comparison of various products should be based on the relative amounts of the chemicals required to be effective and not on advertised claims for the products.

Table IX. Concentrations and times required for algistatic and algicidal activity of different swimming pool products against Phormidium inundatum (Wis. 1093) (Allen's medium, 300,000 cells/ml).

Chemicals tested	Recommended concentration (initial treatment) (mg/liter)	Concentration required to be algistatic (mg/liter)	Time required for recommended concentration to be algicidal (hours)
Heavy metals:			
Copper sulfate	(20)[a]	2	[b] > 24
Algeeclear	3	3	> 24
Cuprose	10	2	> 24
Silver nitrate	(1)[a]	0.14	> 24
Silver sulfate	(1)[a]	0.08	> 24
Algaedyn	12.5	14	> 24
Phenyl mercuric acetate	(0.15)[a]	0.08	0.15
Algimycin-200	3	1.5	0.15
Algimycin-MT4	3	1.5	0.08
Quaternary ammonium compounds:			
Cetyl trimethyl ammonium bromide	(3)[a]	1	6
Algistat	5	4	12
Exalgae L.C.	5	2	12
Armazide	3	2	24

[a] Concentration tested for algicidal activity.

[b] > means "more than."

Water Cooling Towers

The growth of algae on water cooling towers used in conjunction with power plants and air conditioning units is stimulated by the relatively warm temperatures and increasing concentrations of salts in circulation. Control of these growths is complicated by the fact that the growths of algae are accompanied by compact communities of bacteria, fungi, protozoans, worms and insect larvae. Merely killing the developed growths by occasional applications of biocides would release large quantities of slimy material which could plug up pipes and cause unsightly or even dangerous overflows. It is very important, therefore, that control measures be maintained to prevent such growths.

The chemicals to be used as biocides or biostats under the conditions pertaining to water cooling towers must meet requirements based upon the peculiarities of each installation. For instance, the use of chlorine on wooden towers is discouraged because of its damaging effect on wood. The possible pollution of streams receiving that portion of water which must be constantly bled off for the proper functioning of the cooling tower system will also restrict the use of some potentially effective products. Fitzgerald (1964c) and Wolfson and Song (1964) have presented techniques for the evaluation of potential biocides. Maguire (1956) and Sladeckova (1969) have reviewed some of the approaches to the control of growths on cooling towers.

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Detoxification, Synergism, Fish ponds, Algistatic activity, Algicidal activity

27 Abstract

An evaluation of algicides--what they are, their usage, how they are tested, their efficiency, and methods of application--is presented. Detailed are appropriate test organisms, culture and test media, the importance of algicidal versus algestatic effects, and effective chemical concentrations required to achieve potential toxicity. Characteristics of an algal problem, together with its environment, influence the methodology of application processes as well as detoxification, resistance, and synergism. Algal problems of water supply reservoirs and recreational lakes, fish ponds, swimming pools, and cooling towers are specifically discussed with suggestions for effective application of toxicants for their control. (Auen-Wisconsin)

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